

THE MINERALOGY OF HAFNIUM

O. IVAN LEE

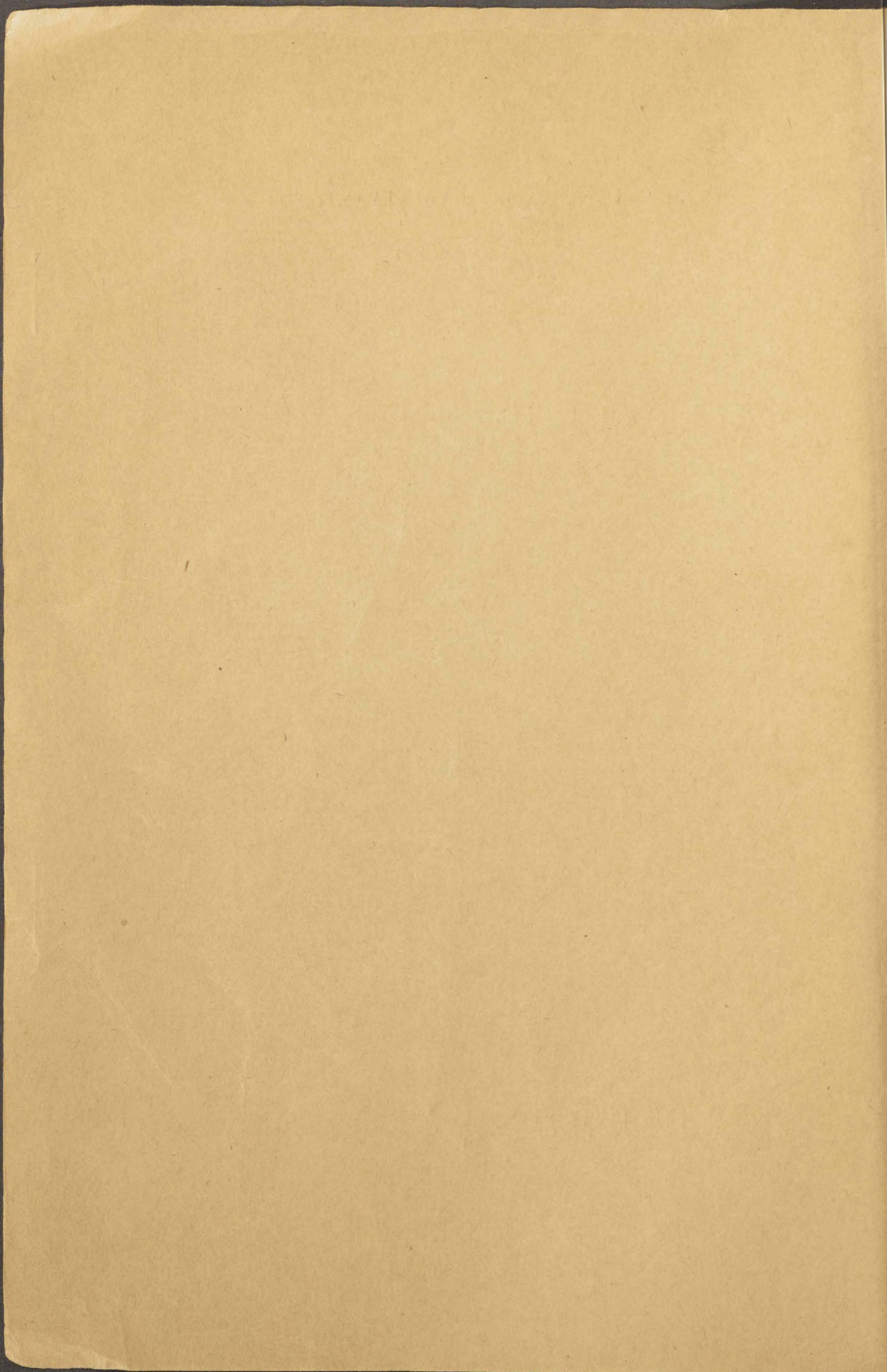
Process Laboratories, Inc., Irvington, New Jersey

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to  
- Captain Thomas I.  
Miller and wife.

With the  
best kind regards and  
the compliments of  
the author.  
O. Ivan Lee







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## THE MINERALOGY OF HAFNIUM\*

O. IVAN LEE

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Although it has been but a scant five years since the advent of hafnium (1), the missing element of atomic number 72, a considerable literature has accumulated, one of the most complete accounts of the element being embodied in the recent monograph by the discoverer, Georg v. Hevesy (44). The papers published, however, have dealt almost exclusively with the chemistry and physics of the metal, and little has been said about the minerals in which it is found. As there are indications that hafnium is emerging from the laboratory to the ranks of the commercial rarer metals, some account of this rather neglected phase of the subject is of general interest and may be of assistance in making the metal more accessible. Inasmuch as elements closely related chemically are often coupled in minerals, as, for example, copper and silver, zinc and cadmium, gallium and indium, germanium and tin, columbium and tantalum, molybdenum and tungsten, and the rare earths, it will be instructive briefly to review the salient facts which led to the association of hafnium with zirconium and its discovery therewith.

### THE RARE EARTHS AND THEIR RELATION TO HAFNIA

Ever since Mendelejeff and Lothar Meyer conceived their periodic arrangement of the elements, certain discrepancies were known but ignored for the sake of the more fundamental harmony. The magnetic triad of iron, cobalt and nickel, and the noble ones of the platinum metals were disturbing, but even more so were that significant group of numerous metals follow-

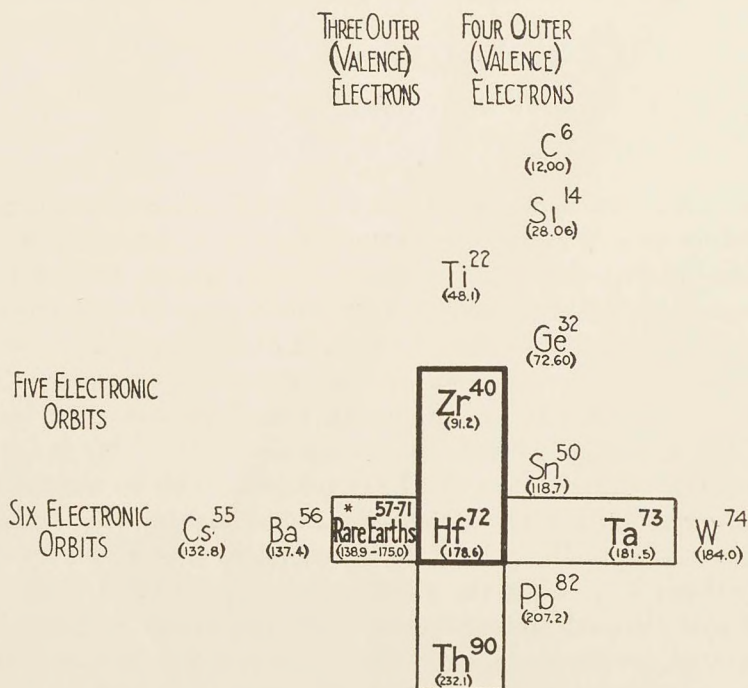
\* Based on a paper presented to the New York Section of the American Chemical Society, December 10, 1926.

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ing barium, known collectively as the rare earths. So far as then known, other triads could follow and new rare earths might



* 57-71 Rare Earths (138.9 - 175.0)	La <sup>57</sup> (138.9)	Ce <sup>58</sup> (140.2)	Pr <sup>59</sup> (140.9)	Nd <sup>60</sup> (144.3)	Il <sup>61</sup> (146.1)	Sm <sup>62</sup> (150.4)	Eu <sup>63</sup> (152.0)
Gd <sup>64</sup> (157.3)	Tb <sup>65</sup> (159.2)	Ds <sup>66</sup> (162.5)	Ho <sup>67</sup> (163.5)	Er <sup>68</sup> (167.7)	Tm <sup>69</sup> (169.4)	Yb <sup>70</sup> (173.5)	Lu <sup>71</sup> (175.0)

FIG. 1. HAFNIUM AND RELATED ELEMENTS ARRANGED ACCORDING TO MOSELEY'S LAW OF ATOMIC NUMBERS<sup>1</sup>

(Atomic weights<sup>2</sup> given in parentheses)

be sought; in a word, no valid limitation could be placed on the number of elements possible, and it might even be greater

<sup>1</sup> After H. D. Hubbard, U. S. Bureau of Standards, Periodic Chart of the Atoms, Pub. W. M. Welch Mfg. Co., Chicago, Ill., 1926.

<sup>2</sup> Berichte 60, 1; 1 (1927), II excepted.



than could be accommodated by the periodic system. Mendelejeff estimated the rare earths as numbering twenty. But Moseley's concept of atomic numbers has demonstrated that there is room for but fifteen, all now known since Hopkins' discovery (2) of element number 61, illinium.

Of the fourteen rare earths known at the time of Moseley's postulation, those with atomic number 70 and 71 were the last discovered. In 1878, Marignac isolated a new earth from the old erbia, slightly more basic, and which was named ytterbium. In 1905, Welsbach found that ytterbium was a mixture of two elements, and in 1907 named them aldebaranium and cassiopeium, and they have since been identified as elements number 70 and 71. Urbain, however, had already confirmed their entity and named them neoytterbium and lutecium, and the names finally adopted in 1914 were ytterbium and lutecium. It was suspected by both Welsbach and Urbain that Marignac's ytterbium contained yet a third element, and both investigators carefully searched for it. Welsbach failed to find any, but Urbain was more successful, and in 1911 announced the discovery of this new rare earth which he called celtium. In 1922, Dauvillier stated that Urbain's preparation showed faint traces of elements number 69 and 72 in addition, indicating in 1923 that element 72 was present in the proportion of about 1:10,000. Meanwhile, Hevesy had taken up the question, and in 1922, by virtue of the quantum theory of atomic structure (3) asserted that element 72 should indeed be a constituent of an "old element," but of "zirconium" and not of "ytterbium" (fig. 1).

PROBABLE ABUNDANCE OF THE MISSING ELEMENT, AND  
RESEMBLANCE TO ZIRCONIUM

It could not be foretold by the pioneer investigators whether element No. 72 was abundant enough in a mineral to be recognized in the specimens to be examined, but there was good reason to believe that the element sought was not rare. For instance, it was known that elements with odd atomic numbers, such as gallium, 31, indium, 49, and thallium, 81, are much more scarce than those with even, such as germanium, 32, tin, 50,



and lead, 82. A study of the relative abundance of silica, titanium, zirconium and thorium in the lithosphere was also reassuring on this point, their oxides being found in the earth's crust in the percentages respectively of 59.09, 1.05, 0.04 and 0.002.

Bohr's theory of atomic structure (3) demanded that element 72 must differ entirely in its outer structure from that possessed by the rare earths which precede it, so that the difference between lutecium and element 72 is greater than that of any two of the rare earths. In addition, its atomic structure shows a very marked analogy to that of element number 40, zirconium. The simultaneous addition of another electron with one more in the outer ring causes element 72 to be quadrivalent. All these considerations gave weight to the belief that element 72 must be analogous to zirconium and therefore likely to be found with it, thus leading to the examination of zirconium minerals and preparations in which the new element was soon identified and isolated.<sup>3</sup> This association is so characteristic that as yet hafnium has not been found other than with the older element discovered by Klaproth in 1789.

The chemical similarity of the two metals is so great that their separation is attended with difficulty, for *hafnium and zirconium exhibit the same chemical reactions*. The fractionation of the hexafluorides makes possible a separation which, while much more difficult than that of columbium and tantalum, is nevertheless easier than most rare earth separations (4).

#### SUGGESTED USE OF CLERICI SOLUTION FOR THE CONTROL OF HIGHER FRACTIONATION

In connection with the resolution of the fluorides of hafnium and zirconium, it occurred to the writer that the little known Clerici solution (5) (6) (7) (8), a molecular mixture of thallium malonate and thallium formate, might be used for testing the

<sup>3</sup> A small sample of the first metallic hafnium ever made, presented by G. Hevesy, the discoverer, is on permanent exhibition at the American Museum of Natural History, New York, in the Element Collection being compiled by G. F. Kunz, Curator of Research.



ammonium hafnium-zirconium hexafluoride crystals with densities too high to float on even fortified methylene iodide, if not soluble or incompatible.

Through the generosity of C. Palache of the Department of Mineralogy, Harvard University, some Clerici solution was placed at the author's disposal, and it was ascertained that ammonium hexafluozirconate floats readily in the diluted solution without sensible solution or decomposition. The only ammonium fluohafniate available appeared in tetragonal instead of monoclinic form, and was possibly heptafluoride. However, it sank in methylene iodide but less readily in the dilute Clerici solution. The finer crystals slowly dissolved, but the coarser ones remained a long time, ample for observation, so that it is believed that this mineralogical reagent should prove useful in advanced hafnium fractionation.

#### THE OCCURRENCE OF HAFNIUM IN NATURE

It will be recalled that in the case of chlorine, no matter from what source it may have been derived, the atomic weight is always the same in spite of the fact that it is a mixture of two isotopes of atomic weights 35 and 37. All the chemical vicissitudes of eons have not disturbed the ratio which was presumably present in the primeval homogeneous mixture. On the other hand, since zirconium and hafnium are chemically separable, some change should have taken place in their original ratio, reflecting in various minerals different geochemical processes in the earth's history. It has been demonstrated that this difference in the ratio of  $\text{HfO}_2$  to  $\text{ZrO}_2$  is a reality, and ranges from 0.007 for the bean-like favas of Brazil to 0.5 for the rare scandium mineral "befanamite" of Madagascar. In general, minerals of granitic origin exhibit a decidedly higher ratio, but the ratios are never so marked as those of less dissimilar elements occurring in pairs such as columbium and tantalum or molybdenum and tungsten. The association of Hf and Zr and other paired elements finds an adequate explanation in the studies of Goldschmidt (9) which support his belief that the geochemical distribution of the elements is conditioned by the electron shell.



TABLE 1  
*List of zirconium minerals known to contain hafnium*  
 (Specific paired analyses are italicized)

NAME	FORMULA	Per cent ZrO <sub>2</sub>	Per cent HfO <sub>2</sub>
Baddeleyite (distinct crystals).....	ZrO <sub>2</sub>	96.5-97.7-98.9	1.2
Syn. Brazilite (fibrous, botryoidal, columnar).....	ZrO <sub>2</sub>	71-93	
Syn. var. (rock) Jacupirangite (crystallized).....	ZrO <sub>2</sub>	59-74-92.4	0.5-0.5-0.7
Zirconia ore	ZrO <sub>2</sub>	71-93	
	ZrO <sub>2</sub> ·SiO <sub>2</sub>	67 80-85	
1. Favas (alluvial pebbles).....	?	75	
Zircon	(Brazilite)	(Na <sub>2</sub> , Ca)O·ZrO <sub>2</sub> ·3SiO <sub>2</sub> ·2H <sub>2</sub> O	0.3
	Zircon	N <sub>2</sub> O·ZrO <sub>2</sub> ·6SiO <sub>2</sub> ·3H <sub>2</sub> O	0.2
Unnamed Zr silicate (orvillite?).....	N <sub>3.13</sub> (CaFe) <sub>6</sub> Cl(SiZr) <sub>20</sub> O <sub>62</sub>	12.20-14.32	0.1-0.2-0.17
	N <sub>3.13</sub> (CaFe) <sub>6</sub> Cl(SiZr) <sub>20</sub> O <sub>62</sub>	12.21	0.2
Catapleite.....	5RTiO <sub>3</sub> ·5RZrO <sub>3</sub> ·R(NbTa) <sub>2</sub> O <sub>6</sub> (R = Ce, Fe, Ca)	29.11	0.6
Elpidite.....	CaNb <sub>2</sub> O <sub>6</sub> ·NaF	29.90	tr.
Eudialyte.....	6CaSiO <sub>3</sub> ·2Na <sub>2</sub> ZrO <sub>2</sub> ·F <sub>2</sub> Ti(SiO <sub>3</sub> )(TiO <sub>3</sub> )	19.80	0.3
Var. Eucolite.....	(SeYt) <sub>3</sub> Si <sub>2</sub> O <sub>7</sub>	2	0.5
Polymignite.....	Sc <sub>3</sub> Si <sub>3</sub> O <sub>7</sub>	1.3	1.0
Pyrochlore.....	13(CaN <sub>2</sub> )O·9SiO <sub>2</sub> ·3ZrO <sub>2</sub> ·Nb <sub>2</sub> O <sub>5</sub>	15.61	0.5
Rosenbuschite.....	ZrO <sub>2</sub> ·SiO <sub>2</sub>	64.23	0.98*
Thortveitite.....	ZrO <sub>2</sub> ·SiO <sub>2</sub>	64.88	1.2
Var. "Pefanamite".....	(Zr, Hf, Th, Be)O <sub>2</sub> ·SiO <sub>2</sub> ·nH <sub>2</sub> O	41.98	4.6
Wöhlerite.....	R <sub>3</sub> Y <sub>2</sub> (Zr, Hf)(SiO <sub>4</sub> ) <sub>12</sub>	52.4	5.5
Zircon.....	3(SiO <sub>2</sub> ·Zr, HfO <sub>2</sub> )·H <sub>2</sub> O	53.2-65.18	3.4-2.6
Var. Hyacinth.....	ZrO <sub>2</sub> ·SiO <sub>2</sub> with Yt, Th, Nb and Ta	49.8	3.5
Alt.	(CaFe)O·2(ZrTiTh)O <sub>2</sub>	51.89	1
Zirkelite.....			

\* Mean value from six analyses.



The hafnium content of virtually every known type of zirconium mineral has been determined, and it has developed that *in the case of zircons, the amount of hafnium is roughly proportional to the radioactivity* (10). The reason for this relation is interesting. The radioactivity is due to uranium and thorium, and hafnium is isomorphous with these elements (11). E. and G. Urbain (12) have discussed the presence of both hafnium and the yttrium elements in some zirconium minerals, and find that the more hafnium is present the larger the proportion of rare earths. Strangely enough, however, hafnium has not been found in any thorium mineral such as thorite or thorianite, nor in titanium minerals like rutile and ilmenite.

#### THE HAFNIUM CONTENT OF THE EARTH'S CRUST

If the average hafnium content of zirconium is assumed to be 3 per cent, the hafnium content of the earth's crust works out to be 1:100,000. Fortunately, nature has made the search easier by segregating the element in certain minerals, among which may be mentioned the following species, varieties and alterations in which hafnium has actually been determined (table 1).

Although numerous zirconium minerals have been investigated for their hafnium content, the field is by no means exhausted inasmuch as the species and varieties enumerated in table 2 are not specifically mentioned as having been tested. Most of these are very rare, and the status of some, such as the varieties of zircon, is not well defined; nevertheless it is of interest and value to test doubtful and even discredited species and varieties as an additional means of checking their validity.

#### THE OCCURRENCE OF HAFNIUM MINERALS IN THE UNITED STATES

Only two zirconium minerals have ever been systematically mined, the ortho silicate, zircon, and in more recent years, the native oxide, brazilite. Only the former occurs in this country and in commercial quantity in but three localities. Zircon was mined intermittently in western North Carolina from 1869 to 1911 (13), as much as 26 tons having been taken out in 1883 by



TABLE 2  
*List of zirconium minerals not reported investigated for hafnium*

NAME	FORMULA	PERCENT OF ZrO <sub>2</sub>
Astrophyllite.....	(KNaH) <sub>9</sub> (FeMnCaMg) <sub>9</sub> (FeAl)[(TiZr)·(OF <sub>2</sub> ) <sub>3</sub> ] <sub>3</sub> [SiO <sub>4</sub> ] <sub>9</sub>	1.21-4.97
Beckelite.....	Ca <sub>2</sub> (YtCeLaNdPr) <sub>4</sub> (SiZr) <sub>3</sub> O <sub>15</sub>	2.5
Chalcoclamprite.....	R <sup>II</sup> Nb <sub>2</sub> O <sub>6</sub> F <sub>2</sub> ·R <sup>II</sup> SiO <sub>3</sub> (R = Ce, Na, Zr and Ca) (allied to pyrochlore)	5.71
Endeioilite.....	R <sup>II</sup> Nb <sub>2</sub> O <sub>6</sub> (OH) <sub>2</sub> R <sup>m</sup> SiO <sub>3</sub> (R <sup>II</sup> = Na <sub>2</sub> , Ca; R <sup>m</sup> = Ce)	3.78
Guarinite.....	3CaSiO <sub>3</sub> ·Ca(FOH)NaZrO <sub>3</sub>	19.70
Hiortdahlite.....	6(Ca <sub>2</sub> Si <sub>2</sub> O <sub>6</sub> )·2[(Na <sub>2</sub> CaH <sub>2</sub> ) <sub>2</sub> Zr <sub>2</sub> F <sub>4</sub> O <sub>4</sub> ] <sub>2</sub> /3[Ca(MgFeMn)(ZrTiSi) <sub>2</sub> O <sub>6</sub> ]	21.48
Johnstrupite.....	Na <sub>3</sub> Ca <sub>3</sub> Ce <sub>2</sub> (FOH) <sub>7</sub> (SiO <sub>3</sub> ) <sub>9</sub>	2.84
Lâvenite.....	Na[ZrOF](MnCaFe)(SiO <sub>3</sub> ) <sub>2</sub>	28.79-28.90
Leucosphenite.....	BaSi <sub>4</sub> O <sub>9</sub> ·2Na <sub>2</sub> (TiZr)Si <sub>3</sub> O <sub>9</sub>	3.5
Loranskite (var. wiikite).....	Tantalate of Yt, Ce, Zr, Fe, etc.	20.00
Lorenzenite (ramsayite).....	Na <sub>2</sub> (TiZr) <sub>4</sub> O <sub>9</sub> ·Na <sub>2</sub> Si <sub>4</sub> O <sub>9</sub>	11.92
Mosandrite.....	Very near johnstrupite	7.43
Nohlite (var. samarskite).....	Hydrated niobate of U, Yt and Fe	2.96
Oliveiraite (alt. euxenite).....	3ZrO <sub>2</sub> ·2TiO <sub>2</sub> ·2H <sub>2</sub> O	63.36
Orvillite (in zircon in "caldasite").....	8ZrO <sub>2</sub> ·6SiO <sub>2</sub> ·5H <sub>2</sub> O	68.04
Riebeckite (arfvedsonite).....	4Na <sub>2</sub> SiO <sub>3</sub> ·5FeSiO <sub>3</sub> ·5Fe <sub>2</sub> Si <sub>3</sub> O <sub>9</sub>	0.75-4.7
Soda-catapleite (var. catapleite).....	Na <sub>2</sub> O·ZrO <sub>2</sub> ·3SiO <sub>2</sub> ·2H <sub>2</sub> O	30.80
Uhligite.....	3·3Ca(TiZr) <sub>2</sub> O <sub>6</sub> ·Al <sub>2</sub> TiO <sub>5</sub>	21.95
Zircon.....	ZrO <sub>2</sub> ·SiO <sub>2</sub>	38-61.53-69
Alt. Auerbachite.....		42.0
Var. "Hagatalite".....		40.9
Var. "Oyamalite".....		



W. E. Hidden (14). More recently, the Pablo Beach deposit of rare minerals on the East Coast of Florida has yielded 2 per cent of zircon sand as an adjunct to the electromagnetic separation of garnet, monazite, rutile and ilmenite. The zircon is stated to swell greatly when ground, disengaging large quantities of helium (15). The occurrence of a rich zirconiferous sandstone near Ashland, Va., has also been described (16). Unfortunately unaltered zircon does not appear to be a promising source of hafnium as the content is usually less than two per cent of  $\text{HfO}_2$ , although a specimen from Henderson County, N. C., is stated to contain more (17). Of the altered zircons, cyrtolite is by far the most common and widely distributed, having been reported from at least seven states—Mt. Antero, Colorado, Branchville, Conn., Rockport, Mass., Mitchell and Henderson Counties, N. C. (three localities) (18), Westchester County, N. Y., Pennsylvania (five localities) (19) and Llano County, Texas, and the Massachusetts and New York minerals have already been shown to be among the richest hafnium minerals known. In addition, a hydrated zircon from Amherst County, Virginia, first described by Mallett (20) is under examination.

The cyrtolite from Texas does not appear to have been analyzed for hafnium as yet, but since it is known to have given "good radiographs after twenty-four hours exposure" (21) it is a fair presumption that the mineral should prove a rich source of hafnia. Hidden and Mackintosh (22) state that it was abundant at the famous Baringer Hill locality during the mining of the yttria minerals, many hundred pounds having been found in a great variety of form and color, but this mine is no longer operated.

The cyrtolite from Rockport, Mass., is high in hafnia (9 to 17 per cent (?)), but very rare, and that from Connecticut and Colorado is also very sparing in occurrence, but the radioactive cyrtolite from Westchester County, New York, has twice been authenticated as high in hafnia and is fully as abundant as the Texas deposit.

#### THE OCCURRENCE OF HAFNIUM NEAR NEW YORK CITY

Up in the hills of Westchester County, near the historic village of Bedford, is a large feldspar mine which has long been a Mecca



for mineralogists from the metropolitan district, since the great pegmatite vein to which the quarry owes its origin, is a prolific and unfailing source of a variety of those minerals which delight the collector. Among these may be mentioned asteriated rose quartz, beryl, columbite, garnet and black tourmaline.

Early in the history of the mine when the workings were not so deep, an unusual, heavy, dark brownish-black mineral of adamantine luster altering to brownish-red or chocolate color of duller aspect, was noticed. It occurred in pockets or isolated



FIG. 2. CYRTOLITE (ALTERED ZIRCON) RICH IN HAFNIA, FROM NEAR BEDFORD, WESTCHESTER COUNTY, NEW YORK

Characteristic curved tetragonal pyramidal crystals are shown penetrating feldspar. This mineral was used by C. James of the University of New Hampshire as the source of the first hafnium and pure zirconium salts prepared in this country (1924). Hafnia: 5.5 per cent (9.5 per cent of  $ZrO_2 + HfO_2$ ). Zirconia: 52.4 per cent. Natural size.

vugs in contact with both smoky quartz and orthoclase, intimately associated with yellowish secondary uranium minerals, one identified as autunite. The presence of these, coupled with the black color, unusual weight and pitchy luster, and tests for uranium, led to the mineral being mistaken for pitchblende or uraninite, then attracting considerable interest because of the recent discovery of radium.

L. V. Case of Tarrytown, N. Y., the original finder, submitted specimens to the department of mineralogy of Columbia University, New York, and Luquer (23) published a paper



showing that the strange mineral was not pitchblende, but the altered zircon known as cyrtolite. It is characterized and named because of the curved form of its crystals, which are tetragonal pyramids not infrequently resembling rhombic dodecahedrons (fig. 2). The unaltered black portions of higher density were found to contain minute lacunae of uraninite, thus accounting for the uranium tests and alteration products, one of which was identified as uraconite, a mineral new to this locality. Striking radiographs are easily made with it (fig. 3), a fact of

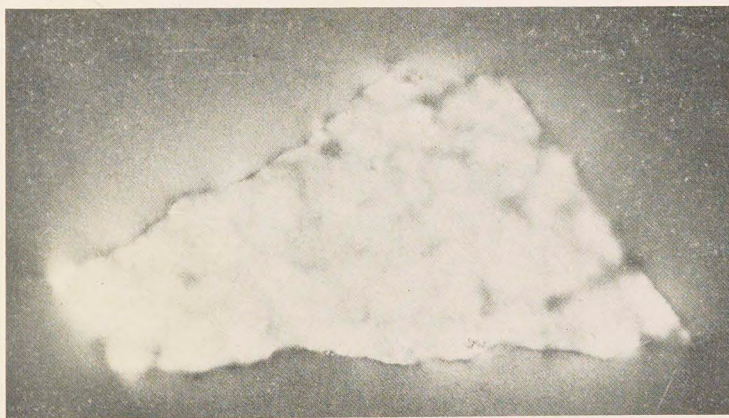


FIG. 3. RADIOGRAPH OF HIGHLY HAFNIFEROUS CYRTOLITE, NEAR BEDFORD, WESTCHESTER COUNTY, NEW YORK

Hafnia: 5.5 per cent (9.5 per cent of  $ZrO_2 + HfO_2$ ). Zirconia: 52.4 per cent. Exposure: 22 days on bare plate. Courtesy of T. I. Miller, Newark Mineralogical Society, Newark, N. J.

especial practical significance to the prospector and mining engineer. A rough analysis of the cyrtolite showed 27.24 per cent of silica, 53.56 per cent of zirconium oxide, and 1.14 to 4.35 per cent of uranium oxide, together with traces of copper, calcium, manganese, "*and probably of yttrium.*" An exact analysis was not considered advisable because of the altered character of the mineral.

About four years ago, the author recalling the statement italicized above, suggested to C. James of the University of New



Hampshire, that the suspected yttria might warrant detailed study, a fifteen pound sample of the mineral subsequently being forwarded. An investigation by him revealed that the presence of yttria, erbia, thulia, etc. was transcended by a notable percentage of the new element hafnium, approximately 10 per cent of hafnium oxide being present in the mixed  $\text{HfO}_2 + \text{ZrO}_2$  as obtained

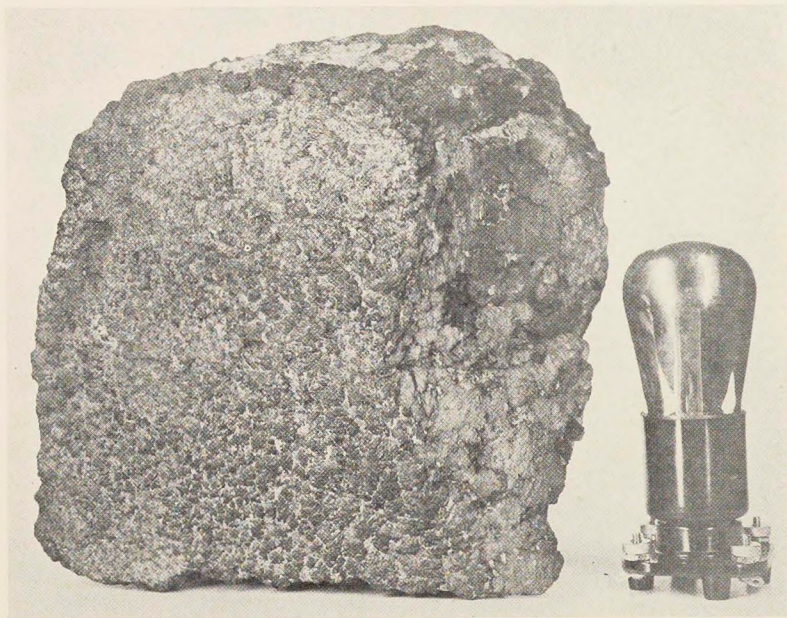


FIG. 4. LARGE SPECIMEN OF HIGHLY HAFNIFEROUS CYRTOLITE, NEAR BEDFORD, WESTCHESTER COUNTY, NEW YORK

Weight: 7.5 kgm. (16.5 pounds). Hafnia: 0.41 kgm. (0.91 pounds). (A standard radio tube is shown for comparison.)

from the mineral (24). In a later letter from Hevesy (25), James' original analysis was confirmed in that a preliminary analysis "very near to the final value" showed 9.5 per cent of hafnium oxide in the mixed zirconium-hafnium oxides which total 52.44 per cent. Unlike the Norwegian alvite, this unusual percentage of the New York mineral appears to be rather consistently maintained, although the yttrium earths are very variable, and a large



quantity was afterwards successfully worked up by James for hafnium and the concomitant zirconium. This is believed to have constituted the first production of these elements in this country.<sup>4</sup> With the possible exception of the Rockport cyrtolite<sup>5</sup> the mineral occurring at Bedford is apparently the richest ore of hafnium yet reported (44). Although the deposit is of limited extent, specimens weighing ten or twelve pounds are not uncommon, and one is illustrated which perhaps contains more hafnium for its size than any other extant (fig. 4).

#### FOREIGN DEPOSITS OF HAFNIUM

Abroad, the principal commercial occurrences of zircon are in the monazite sands of Travancore, India, and of Brazil, and in the pegmatites of Southern Norway, but the mineral has largely lost its former importance as a source of zirconia because of the discovery of the native oxide, baddeleyite. The pure crystallized mineral has been known for thirty-five years, and has been reported from Ceylon, Italy, Sweden and Montana, but it remained for the Brazilian states of Minas Geraes and São Paulo to disclose to the world in 1915, zirconia ore in unprecedented quantity (26). The ore (fig. 5) outcrops on a mountainous plateau, and the methods of mining and transportation employed are very primitive owing to the distance from railroads and the rugged character of the region. Isolated boulders have been found weighing as much as  $27\frac{1}{4}$  milliers (thirty tons), so that such a "specimen" would presumably contain from 136 to 190 kgm. (300 to 420 pounds) of hafnium oxide.

A third hafnium mineral of considerable interest is the com-

<sup>4</sup> Specimens from G. Hevesy of the first hafnium and pure zirconium salts ever isolated, and of the first made in America, from C. James, may be seen in the Chandler Chemical Museum of Columbia University, New York, with related exhibits of historic interest, including Bedford cyrtolite from which the American salts were produced, and a cast lead dish used in their fractionation.

<sup>5</sup> A reprint of "Recherches sur les propriétés du hafnium" (København, 1925) received by the author from G. Hevesy contained the marginal annotation against the hafnia content of 17 per cent reported for analysis 23 (Cyrtolite, Rockport, Mass., U. S. A.), "Uncertain! Must be repeated." This is the same mineral previously reported (G. Hevesy and V. T. Jantzen, J. Chem. Soc. **123**, 3218 (1923), analysis 20) as giving 9 per cent of HfO<sub>2</sub>.



plex eudialyte (and var. eucolite) reported in the United States only from Arkansas (27) and whose occurrence in Hibina-Toundra and Lujavr-urt in the Kola Peninsula of Russian Lapland was recently described by Fersman (28).

In spite of the trying nature of the district—1200 meters above sea level, covered with forests and swamps, infested with insects, devoid of roads, paths or habitations, with snow falling as early as August 9th—the Mineralogical Museum of the Academy of Sciences of the USSR, and the Research Institute of the North have sent six expeditions to this inhospitable country to collect the rare and unique minerals found there in

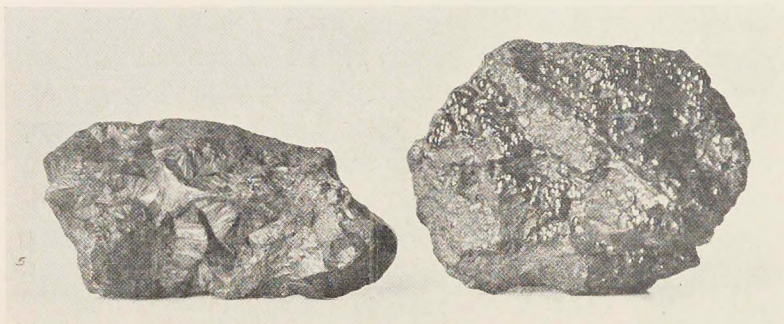


FIG. 5. LOW GRADE HAFNIA ORE ABUNDANT IN BRAZIL. FIBROUS AND BOTRYOIDAL BRAZILITE (BADDELEYITE), CALDAS REGION, STATES OF MINAS GERAES AND SÃO PAULO

Hafnia: 0.5-1.2 per cent. Zirconia: 71-93 per cent. Natural size

profusion. Over five tons of specimens have been collected and are now in part displayed in Leningrad. Among them are about a dozen of the rarer zirconium minerals. Only the eudialyte has been analyzed for hafnium as yet so that this field is a virgin one.

Gordon (29), however, in his description of the noted cryolite mine at Ivigtut, Greenland, notes that eudialyte is of common occurrence in the alkaline syenites about the Tunugdliarfik and Kangerdluarsuk fiords of the Julianehaab district; and 55 tons were collected for technical purposes according to K. J. V. Steenstrup (30). It occurs disseminated in the rock as well as



in veins, and Gordon remarks, perhaps prophetically, that "this district should become an important producer of this mineral if a use for it is ever discovered." A typical specimen of this rare species from this remote locality is illustrated in Figure 6.

It is unfortunate that all of the three minerals aforementioned which are known to be abundant at favored but inaccessible localities, should be so lean in hafnia, even zircon seldom exceeding 1.2 per cent. In this connection, it is well to remember that James (31) has pointed out that *so long as one has a use for*

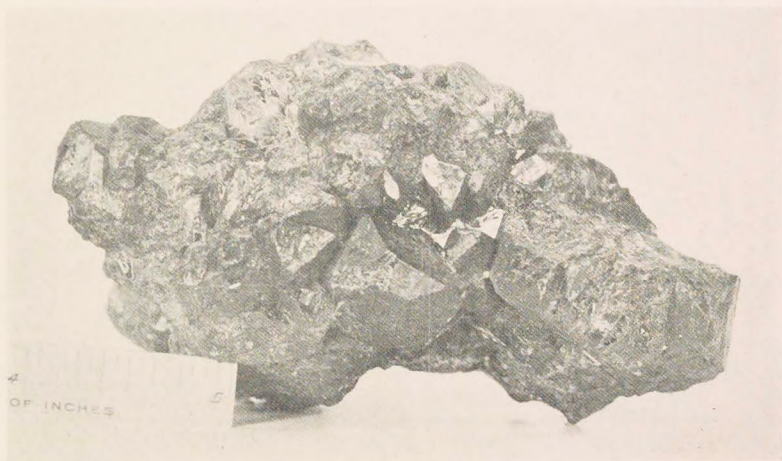


FIG. 6. A RARE AND COMPLEX HAFNIUM MINERAL COMMON IN SOUTHERN GREENLAND. TYPICAL CRYSTALLIZED EUDIALYTE FROM KANGERDLUARSUK  
Hafnia. 0.17 per cent. Zirconia: 14.3 per cent. Natural size

*pure zirconium material, zirconia of very low hafnia concentration can be utilized.* From a strictly scientific viewpoint, the properties of pure zirconium, contaminated as it was for one hundred and thirty-four years, should claim equal attention with those of the offending hafnium, known for only five. Nevertheless, since commercial and historical zirconium preparations examined by Hevesy and others contained only small percentages of hafnium, the general properties already chronicled for the older element do not exhibit marked divergences from those found for



TABLE 3  
The occurrence of hafnium minerals by countries

LOCALITY	MINERAL	ZrO <sub>2</sub>	HfO <sub>2</sub>
<i>Africa:</i>			
Diego Suarez.....	Zircon		0.8
Madagascar.....	Zircon		0.9
Madagascar.....	Grey zircon		0.8
Madagascar, Befanamo.....	"Befanamite" (thortveitite)	1.3	1.0
Madagascar.....	Malakon (alt. zircon)	53.2	4.
<i>Asia:</i>			
Ceylon.....	Beccarite (var. zircon)		2.1
Ceylon.....	Reddish-brown zircon		2.7
Ceylon.....	Zirkelite	51.89	1.
India (Travancore?).....	Zircon from monazite	64.0	1.2
Japan, Mino.....	Naëgite	48.30	7.
Japan, Naegi.....	Naëgite	49.8	3.5
Slam, Province of Chantaboon.....	Zircon (transparent blue)		4.?
<i>Australia:</i> No minerals have yet been definitely reported from the continent as containing hafnium.....			
Tasmania.....	Zircon		*
Tasmania.....	Greyish brown zircon		1.1
<i>Europe:</i>			
Austria, Carinthia.....	Zircon (transparent white)		4.?
France, Espailly (Le Puy).....	Zircon (var. hyacinth; transparent red)	64.83	1.2
France, Espailly (Le Puy).....	Zircon (var. hyacinth; transparent red)		0.7
France, Espailly (Le Puy).....	Zircon (transparent green)		1.1
Italy, Lonedo.....	Zircon (yellow)		0.7
Italy, Lonedo.....	Zircon (red)		0.7



Italy, Vicenza.....	Zircon (transparent green)		0.8
Italy, Vesuvius.....	Zircon		0.7
Norway, Barkevik.....	Eudialyte (var. eucolite)	14.47	0.7
Norway, Barkevik.....	Eudialyte (var. eucolite)	12.21	0.2
Norway, Barkevik.....	Wöhlerite	15.61	0.5
Norway, Brevik.....	Zircon		1.0
Norway, Brevik.....	Reddish-brown zircon	63.2	1.0
Norway, Frederiksvärn.....	Polymignite	29.11	0.6
Norway, Frederiksvärn.....	Brown zircon	65.2	1.0
Norway, Gjersted.....	Alvite (alt. zircon)		9.
Norway, Iveland.....	Thortveitite	2	0.5
Norway, Hitterö.....	Malakon (alt. zircon)	65.18	2.6
Norway, Kragerö.....	Alvite (alt. zircon)	41.98	4.6
Norway, Kragerö.....	Alvite (alt. zircon)		3.
Norway, Kragerö.....	Alvite (alt. zircon)		8.
Norway, Kragerö.....	Alvite (alt. zircon)		15.
Norway,.....	Catapleite	31.52	0.3
Norway, Langesund.....	Brown zircon		1.7
Norway, Langesund.....	Rosenbuschite	19.80	0.3
Norway, Larvik.....	Greyish brown zircon		6.
Norway, Risør.....	Alvite (alt. Zircon)		10.
Norway.....	Grey syenite (rock)		3.8
Norway, Unneland.....	Thortveitite	0.8	1.1
Sweden, Alno.....	Pyrochlore	2.90	tr.
Russia, Miask.....	Greyish brown zircon	64.22	1.1
Russia, Rojkow Kliutsch, Ural.....	Brown zircon		0.5
Russia, Kola.....	Eudialyte (red)		0.1
<i>North America:</i>			
Canada, Eganville, Ont.....	Brown zircon		1.2
Canada, Renfrew County, Ont.....	Zircon		0.6



TABLE 3—Continued

LOCALITY	MINERAL	ZrO <sub>2</sub>	HfO <sub>2</sub>
<i>North America—Continued:</i>			
Greenland.....	Zircon		0.8
Greenland.....	Catapleite	31.53	0.3
Greenland, Narsarsuk.....	Elpidite	20.28	0.2
Greenland, Narsarsuk.....	Reddish-brown zircon		0.8
Greenland, Narsarsuk.....	Eudialyte (red)	12.20	0.2
Greenland, Narsarsuk.....	Eudialyte (brown)	12-16	0.6
Greenland, Kangerdluarsuk.....	Eudialyte	14.32	0.17
United States, Connecticut.....	Zircon		1.0
United States, Rockport, Massachusetts.....	Cyrtolite (alt. zircon)	40.	9.
United States, Rockport, Massachusetts.....	Cyrtolite (alt. zircon)	44.	17. (?)
United States, Bedford, New York.....	Cyrtolite (alt. zircon)	52.4	5.5
United States, North Carolina.....	Grey zircon		4. (?)
United States, North Carolina.....	Brown zircon		1.3
United States, North Carolina, Henderson County.....	Zircon		4.0 (?)
<i>Oceania:</i> No minerals have yet been reported definitely as containing hafnium.			
<i>South America:</i>			
Brazil.....	Baddeleyite	97.7	1.2
Brazil.....	Fava	92.42	0.7
Brazil.....	Fava (shell)	59.	0.5
Brazil.....	Fava (nucleus)	74.	0.5
Brazil.....	Zircon separated from monazite sand	64.	0.4
Brazil, Caldas.....	Zircon		1.8
Brazil, Minas Geraes.....	Zircon		1.0

\* "Very considerable."



hafnium-free zirconium preparations. On the other hand, the properties of hafnium are very remarkably different from those of zirconium, so that interest has naturally centered in the newer element and the minerals richest in it.

Of the altered zircons, cyrtolite is known in India, Madagascar, Italy, Sweden and Hybla, Ontario, and Norwegian alvite has been useful to the early investigators of hafnium, but does not seem to be a common mineral.

For the guidance of those interested, table 3 presents the distribution of zirconium minerals whose hafnium content has been definitely determined (32) but the list can ultimately be made far more comprehensive as more analyses accumulate.

It is to be feared that the prospector and the mining engineer will be compelled for some time to come to rely on well equipped chemists of skill and experience for authentic information concerning the actual hafnium content of suspected minerals and ores. Meanwhile, it may be useful to point out that since the various types of altered zircon which have proven richest in the new element, are pseudomorphic after zircon, it is not difficult to become accustomed to recognizing their square pyramidal form, particularly if specimens of the various alterations of zircon are studied. If such a mineral is identified and found to be in addition markedly radioactive, it is reasonably certain that the mineral under examination will prove to contain an appreciable percentage of hafnia.

#### CONCLUSION

In conclusion, it must not be forgotten that the discovery of hafnium has necessitated the revision and correction of all the data on zirconium so painfully acquired over the course of a century and a third. The International Critical Tables warns that "All zirconium salts (are) probably contaminated with 1-5 per cent of hafnium" (33). So far as hafnium is concerned, it is somewhat early to ask for what practical purpose it may ultimately prove singularly appropriate, for the process of accumulating and studying facts about it is still actively engaging the attention of many chemists and physicists. An excellent



summary of the commercial uses of zirconium set forth by Meyer (34) will be found very suggestive, however, to those of a pragmatic turn of mind. It may be of interest also, to note that the close similarity of metallic hafnium to thorium coupled with its high melting point and electronic emissivity (35), have already led to patents being taken out for its use in lamp filaments, particularly those used in radio tubes (36).

The author extends his sincere thanks to G. Hevesy of the Physikalischchemisches Institut of the University of Freiburg, Germany, and to C. James of the Department of Chemistry of the University of New Hampshire, Durham, N. H., for their cordiality and helpful coöperation in supplying numerous items of interest embodied in this article.

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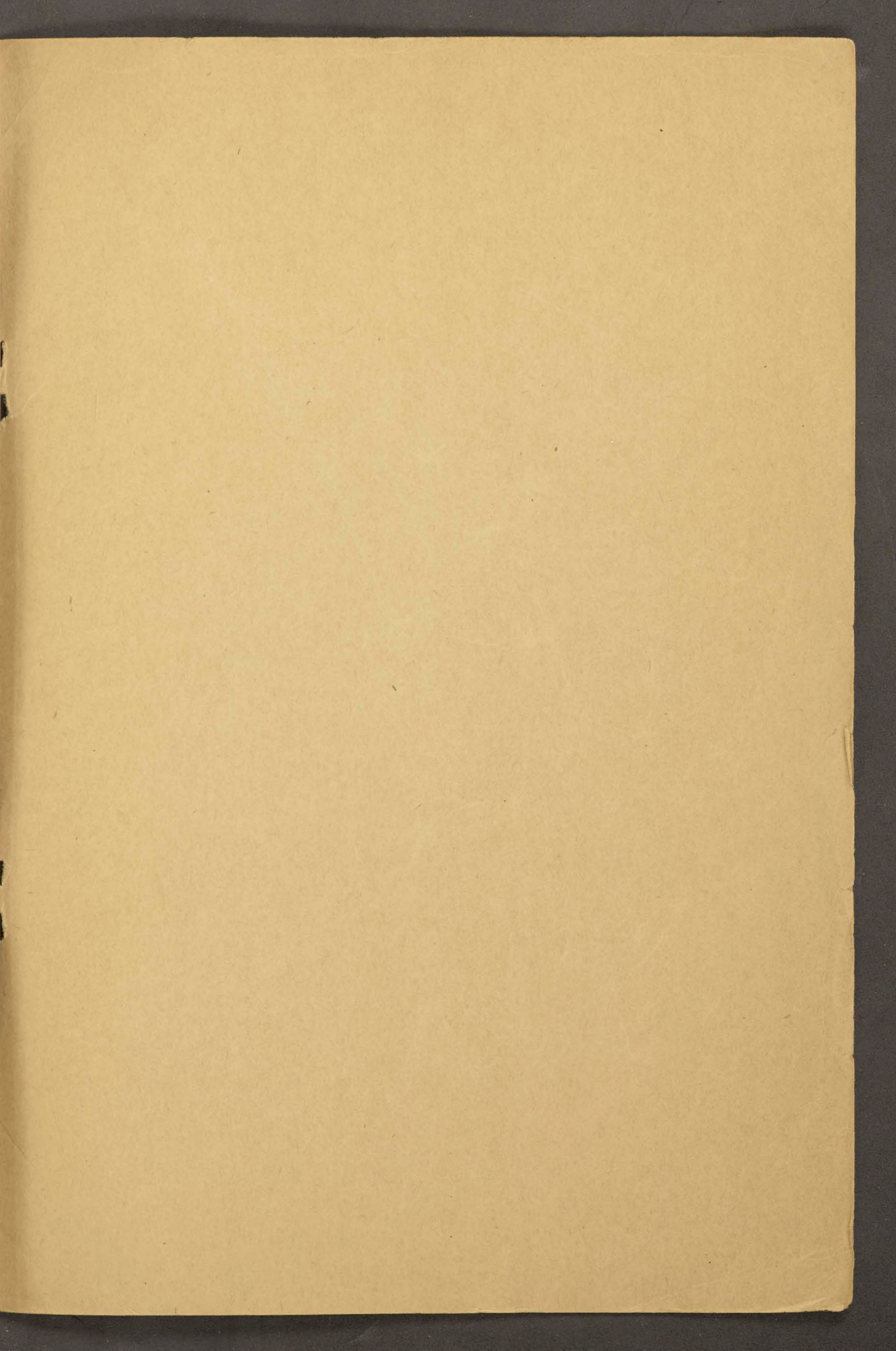
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## WHO FOUND HAFNIUM?

IT'S A WISE SON who knows what his mother Earth is made of. The old alchemists knew of only a few "elements" and they spent most of their time trying to transmute the baser ones into gold, instead of analyzing the substance of earth to isolate the different things in it. In more recent times scientists have made out that there are ninety-two possible chemical elements. In discovering new elements the solar spectrum and later the X-ray spectrum have been of great help to the chemist. For instance, helium, which was discovered in the sun—from which it is named—in 1868 by lines observed in the solar spectrum, was not isolated by the chemist Sir William Ramsay until 1895. Now comes what the scientists consider the most striking chemical event since Ramsay's isolation of helium, in the discovery of a new element called hafnium. Scientists have been looking out for this new element to fill the gap in the list of possible elements and its discovery is claimed by scientists of several nations who have been working simultaneously on the problem. The London *Times* reports that Dr. Alexander Scott of the British Museum isolated the element and was recently able to show specimens of the oxid, a cinnamon colored powder, to a crowded meeting of the Chemical Society, to state its atomic weight and describe its chemical nature. As the New York *Times* informs us:

"In 1913 Dr. Alexander Scott received for analysis samples of a black sand from New Zealand from which he extracted a cream-colored sand containing 75 per cent. of magnetic oxid of iron and 25 per cent. of titanium dioxide. In further tests on the titanium dioxide he always found small quantities of a highly refractory residue. He continued to collect these, labeling them a new oxid, but until a fortnight ago had never had time to pursue his investigations.

"Knowing from the similarity of the compounds it made with potassium and fluorin to those of titanium and zirconium that it was likely to be a candidate for place 72 in the atomic table of elements, he began to work as soon as he heard of the discovery by Coster and Hevesy of Copenhagen. By a series of determinations he ascertained the atomic weight to be approximately 180 and the chemical characters to be those which X-ray spectroscopy would assign to hafnium. It would have been easy to apply the X-ray method to his oxid, says *The Times*, but by an act of international courtesy he has written to Coster and Hevesy offering to send them the necessary material for the purpose."

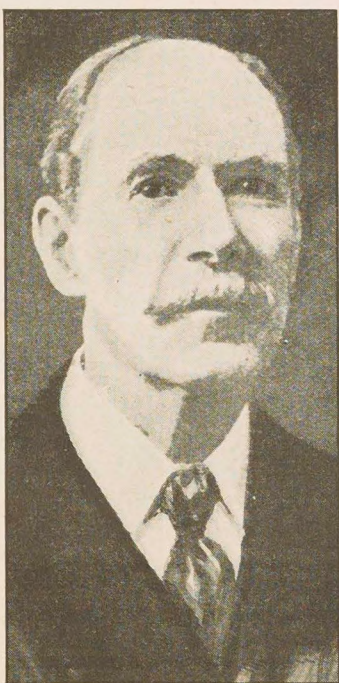
More information about hafnium and its discoverer is contained in paragraphs quoted from the London *Times*, which says:

"The black sand deposit in New Zealand is stated to be more than seven miles in length and of unknown depth, so that if hafnium turns out to have a commercial value, it can be produced in bulk. From its analogies to titanium and zirconium it may be of value in the making of incandescent mantles.

"Dr. Scott thinks it rather unfortunate that a geographical name, hafnium (Copenhagen) should have been given to the new element and partly in jest, suggested that as it was allied to titanium (Titania), an appropriate name would be oberonium.

"Dr. Scott is at present Director of Scientific Research at the British Museum, and is specially known for his investigations on the chemical deterioration of museum objects and the ways of restoring them. He is constantly consulted by Lord Carnarvon over the preservation of the relics from the tomb of Tut-ankh-Amen.

"He received warm congratulations from the Chemical Society on his brilliant work, the most striking chemical event since Ramsay's isolation of helium."



HE ISOLATED HAFNIUM.  
But Dr. Alexander Scott of London may have to share the credit with French and Danish scientists.

That the newly discovered element is one of six for which chemists have been looking, and that claimants of two nationalities dispute the honor of discovery with those mentioned above, we are told by Science Service's *Daily Science News Bulletin* (Washington). We read:

"The disputed position in the periodic table of chemical elements is known as number 72. Prof. G. Urbain of the Sorbonne announced some years ago that he had identified and isolated a new rare earth element that he called 'celtium' as a tribute to the French or Celtic race. Prof. A. Dauvillier within the last few months has announced to the Paris Academy of Sciences that he finds by X-ray spectroscopy of rare earth mixtures that Urbain's celtium fits into the gap in the known elements where number 72 should be.

"But from Denmark comes the counter claim that element 72 is not a rare earth metal, like cerium and thorium whose oxides are used in gas mantles, but an element very similar to the metal zirconium. Coster and Hevesy have investigated the spectrums obtained when extractions from zirconium minerals are made to produce X-rays, and they have found lines in the resulting spectrum, hitherto unknown, that correspond to those that element number 72 should have. But the lines found by these Danish scientists are not the same as those found by the French physicist and chemist. The Danes have patriotically proposed that the new element they have announced be named 'hafnium,' derived from Hafniæ, meaning Copenhagen.

"If the discovery of Drs. Coster and Hevesy is confirmed, hafnium may some time be found in considerable quantities, as they report that 'in a Norwegian zirconium mineral the new lines were so intense that we estimate the quantity of the element in it to be at least equal to one per cent.

"If, on the other hand, the claims of Urbain and Dauvillier are substantiated by time, Professor Urbain will have the credit of discovering two of the 92 possible chemical elements, a unique distinction. He previously discovered and isolated Lutecium, naming it in tribute to his native city, Paris, known in ancient times as 'Lutecia.'

"Many of the chemical elements have been first discovered in the spectrum and then found and isolated by chemical means. Helium was discovered in the sun in 1868 by lines seen in the solar spectrum, and not until 1895 was it isolated by Sir William Ramsay. The X-ray spectrum of a substance under investigation is much more certain of interpretation than an ordinary light spectrum because the positions of its lines are directly and simply related to the arrangement of its elements in what is called the 'periodic table.' Moseley, the young British physicist who was killed early in the war, was able by applying X-ray spectroscopic methods to arrange the known chemical elements in an orderly series according to their atomic numbers. This classification is much more enlightening than the periodic table devised by the Russian chemist, Mendeleef, in 1869. Moseley's work showed that there are spaces for several elements that man does not yet know, and among them was number 72. Numbers 43, 61, 75, 85 and 87 are still missing, but by their positions in the series, scientists have predicted the properties of the unknown elements. The position of 72 in the series is such that it must be related both to the rare earth metals and to the metal zirconium, so that theoretical data do not help in deciding the present scientific controversy."

That discoveries of new members in the list of so-called "rare earth" metals may be expected is well known to students of chemistry. We are reminded in Raphael Meldola's "Chemistry" that:

"The known metals of this group exist as compounds in a complex mixture of minerals known as monazite sand, found in various parts of the world, which is worked up on the large scale for the manufacture of the mantles used as incandescent gas-burners. These mantles are composed mainly of the oxides of thorium and cerium, supported by a suitable framework."